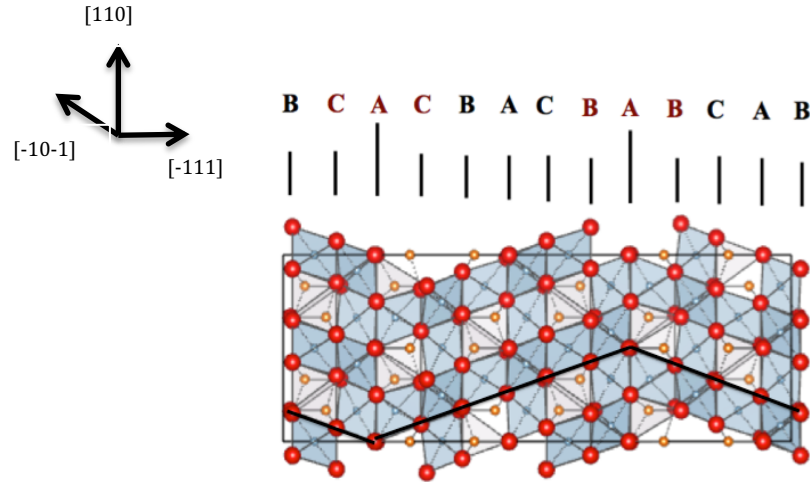## Supplementary information and data

1.0 Supercell

Figure R1: 336-atom spinel supercell with (111) twin planes. Red atoms- O, Yellow atoms- Mg, Blue atoms-Al

2.0 Equation-of-state fits and Vibrational free energy

The ground state total energy as a function of volume is fitted using the widely used Birch-Murnaghan EOS [Birch 1947; Birch 1978]. Their four parameter EOS is given by the equation (1). The E-V data of the supercells with and without twins are calculated between -5 to 4 vol% with a step size of 1 vol%.

(1) $E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2}$

where *a, b, c,* and *d* are the fit parameters.

The Debye temperature Θ_D within the Debye-Gruneisen approach can be calculated from the properties obtained from the ground state equation of state (EOS) and is defined as follows [Slater 1939],

(2) $\Theta_D = sAV_0^{1/6}\left(\dfrac{B_0}{M}\right)^{1/2}\left(\dfrac{V_0}{V}\right)^{\gamma}$

where γ is the Gruneisen constant describing the anharmonic effects of the vibrating crystal lattice and can be approximated either based on Slater [Slater 1939] or Dugdale and Macdonald [Dugdale and Macdonald 1953] expressions as given by

$\gamma = [(1 + B_0')/2 - x]$. Here 'x' is an adjustable parameter and is 2/3 for high temperature and 1 for low temperature case. 's' is the scaling factor and for non-magnetic cubic metals with an assumption of average sound velocity, this factor is determined as 0.617 by Moruzzi et al. [Moruzzi et al. 1988]. In this work with $MgAl_2O_4$ we estimated a scaling factor of 0.88 by using second moment Debye temperature, which is calculated from the firs-principles predicted phonon density of states of the pristine phase. 'A' is a constant as given by $A = (6\pi^2)^{1/3} h / k_B = 231.04$, V is volume in Å^3, B_0 is the bulk modulus in GPa and M is the atomic/molecular weight. The B_0 and V_0 in the equation (2) are obtained from the EOS fit.

The vibrational free energy can be calculated from the Debye temperature as given by the equation (3),

$$(3) \qquad F_{vib}(V,T) = \frac{9}{8} k_B \Theta_D + k_B T \left\{ 3 \ln \left[1 - \exp \left(-\frac{\Theta_D}{T} \right) \right] - D \left(\frac{\Theta_D}{T} \right) \right\}$$

where $D\left(\frac{\Theta_D}{T} \right)$ is the Debye function, which is given by $D(z) = 3/z^3 \int_0^z t^3 / [\exp(t) - 1] dt$

The inversion free energies as given by $\Delta G_{inv}^{111}(T) = \Delta H_{inv}^{111} - T(\Delta S_{vib}^{111}(T) + S_{conf}^{111})$, are obtained after incorporating the vibrational and configurational contributions to the free energy. The S_{conf}^{111} on the M-layer within the twinned region is calculated for random configuration of Al and Mg after inversion. The ΔH_{inv}^{111} at any given percentage of inversion is taken for the most stable inverted configuration on the M-layer as shown in Figure 3. Interestingly, one of the 6 configurations that are possible at 50% inversion on M-layer, transitioned to 75% inversion during the relaxation calculation. This aspect pertaining to the mechanism of inversion near the twin plane and within the pristine bulk region will be reported in a separate manuscript in future.

3.0 Calculations using Ginzburg-Landau rate law

The $\frac{d\Delta G}{dQ}$ in equation ($\frac{dQ}{dt} = -\frac{\gamma \exp\left(-\frac{\Delta H^*}{RT}\right)}{2RT}\left(\frac{d\Delta G}{dQ}\right)$) is approximated to be a constant (82876 J/mole) in the whole temperature range after examining the $\Delta G_{inv}^{111}(T)$ at different percentages of inversion on the M-layer (Figure 5b). The hcp-twinned region (with ACA packing is treated as a twinned-phase of MgAl$_2$O$_4$-stoichiometry, to estimate the thermodynamic driving force for the inversion on the M-layer within this region.

Reference cited

Moruzzi, V.L, Janak, J.F. and Schwarz, K. (1988) Calculated thermal properties of metals. Physical Review B, 37, 790-799